

Surface Structure Determination Using Simplified Physics Surrogates



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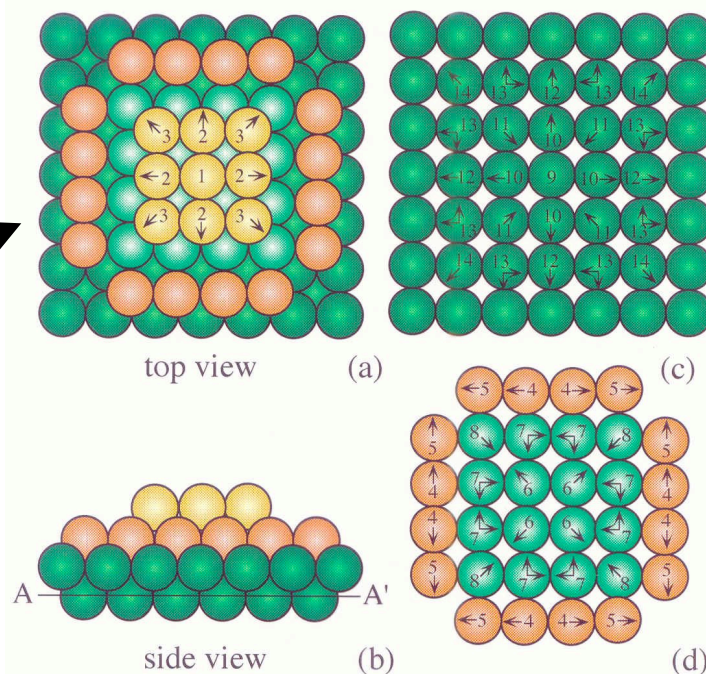
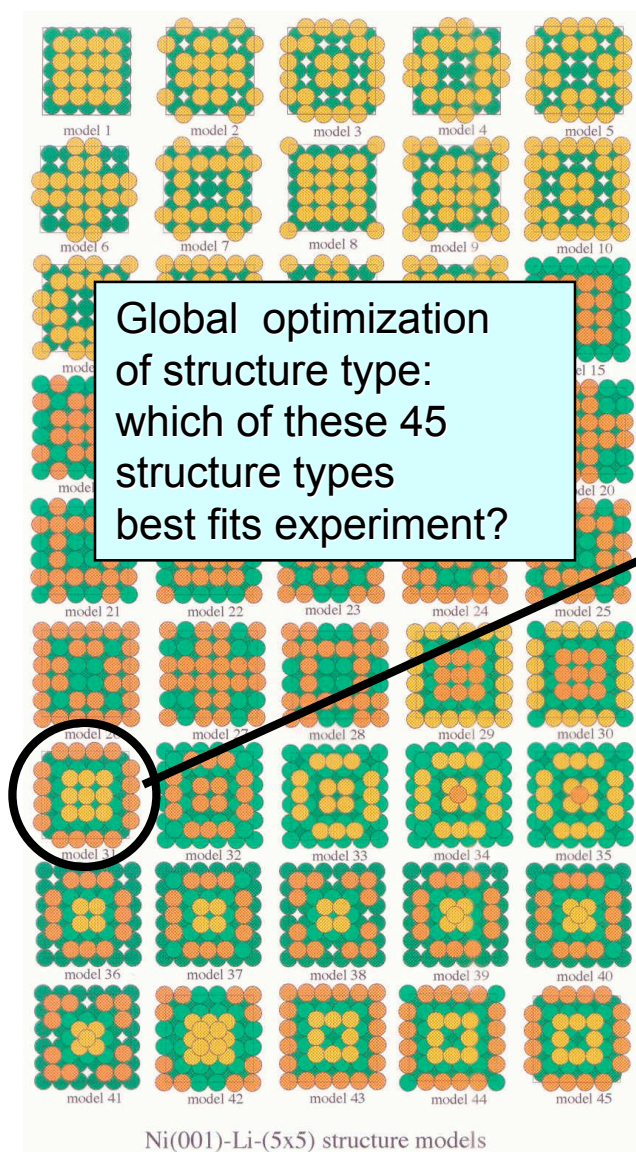
C O M P U T A T I O N A L R E S E A R C H D I V I S I O N



Surface structure determination from experiment

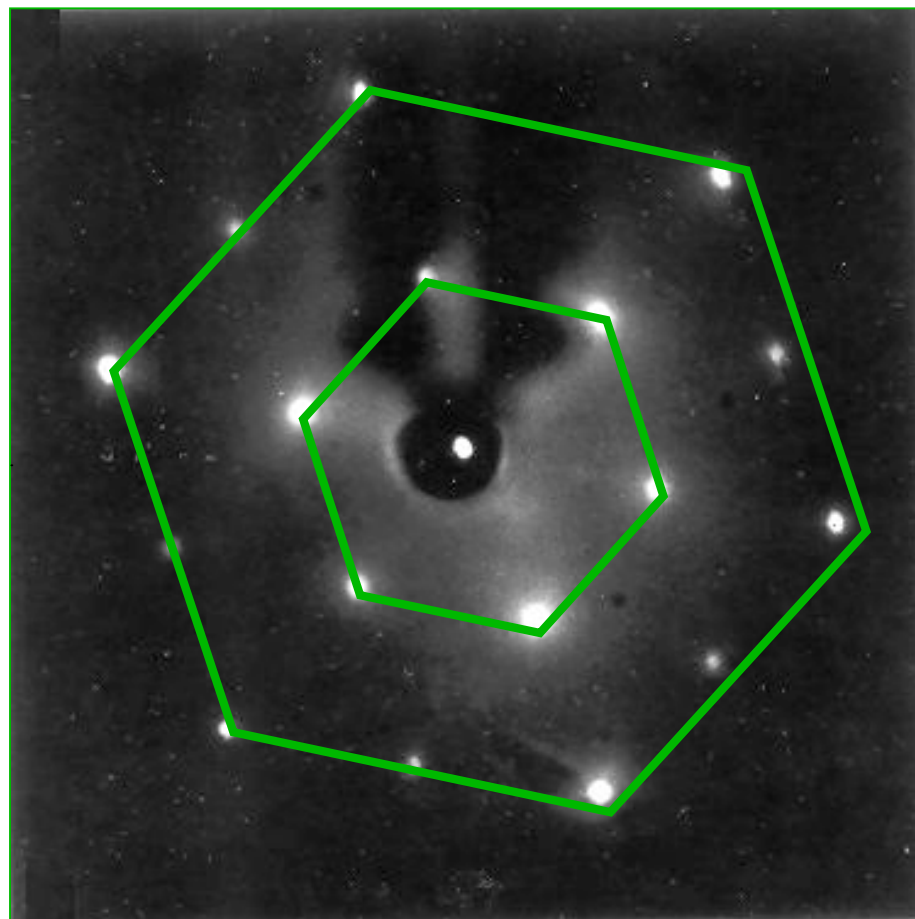
- ❖ Electron diffraction determination of atomic positions in a surface:
 - Li atoms on a Ni surface

Global optimization of structure type: which of these 45 structure types best fits experiment?



Local optimization of structure parameters: which are the best interatomic distances and angles?

Low-energy electron diffraction (LEED)



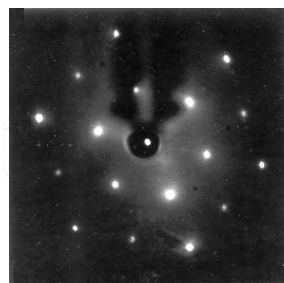
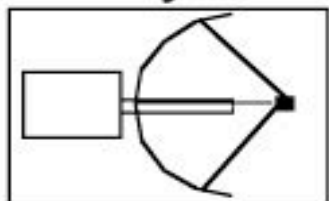
Low-energy electron diffraction pattern due to monolayer of ethylidyne attached to a rhodium (111) surface

- ❖ Goal is to determine surface structure through low energy electron diffraction (LEED)
- ❖ Need to determine the coordinates and chemical identity of each atom
- ❖ Non-structural parameters, i.e. inner potential, phase shift δ , thermal effects and damping.

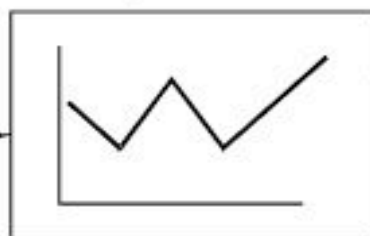
Low Energy Electron Diffraction

Experiment

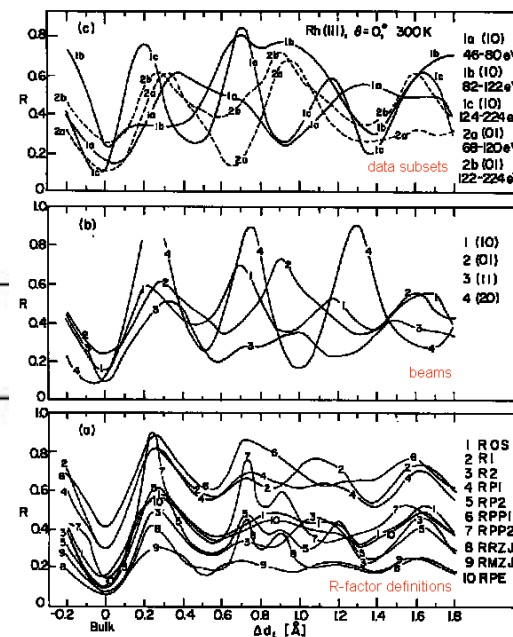
LEED system



I-V spectra



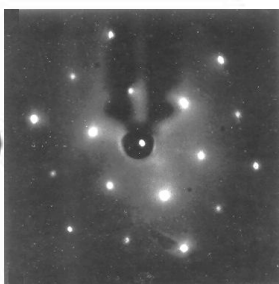
R-Factors



Theory

(x,y,z) input parameters

- 1) (-1.33, -0.08, 2.51)
- 2) (0.33, 0.00, 0.00)
- 3) (1.89, 1.22, 3.51)



I-V spectra



Pendry R-factor

$$R = \sum_g \int (Y_{gth} - Y_{gexp})^2 dE / \sum_g (Y_{gth}^2 - Y_{gexp}^2) dE$$
$$Y(E) = L^{-1} / (L^{-2} + V_{oi}^2),$$
$$L(E) = I' / I, \quad L \approx \sum_j \frac{-2(E - E_j)}{(E - E_j)^2 + V_{oi}^2}$$

- ❖ LEED curves consist for the main part of a series of Lorentzian peaks:

$$I \approx \sum \frac{a_j}{(E - E_j)^2 + V_{oi}^2}$$

- ❖ Their widths are dictated by the imaginary part of the electron self-energy (optical potential):

$$\Delta E = 2|V_{oi}|$$

- ❖ Pendry R-factor emphasizes positions of the maximum and minimum rather than the heights of the intensities

Optimization formulation

- ❖ Inverse problem
 - minimize R-factor - defined as the misfit between theory and experiment
 - Several ways of computing the R-factor
- ❖ Combination of continuous and categorical variables
 - Atomic coordinates: x, y, z
 - Chemical identity: Ni, Li
- ❖ No derivatives available; function may also be discontinuous
- ❖ Invalid (unphysical) structures lead to function being undefined in certain regions and returning “special values”

Previous Work

- ❖ Early attempts used Hooke-Jeeves, nonlinear-least squares, genetic algorithms, ...
- ❖ We've also used pattern search methods (NOMAD)
- ❖ Effective, but expensive
- ❖ Several hundred to 1000s of function calls typically needed
- ❖ Each function call can take up to 2 minutes on a workstation class computer

Global Optimization in LEED Structure Determination Using Genetic Algorithms, R. Döll and M.A. Van Hove, Surf. Sci. 355, L393-8 (1996).

G. S. Stone, MS dissertation, Computer Science Dept., San Francisco State University, 1998.

General MVP Algorithm

1. Initialization: Given Δ_0 , x_0 , M_0 , P_0
2. For $k = 0, 1, \dots$
 1. SEARCH: Evaluate f on a finite subset of trial points on the mesh M_k } Global phase can include user heuristics or **surrogate** functions
 2. POLL: Evaluate f on the frame P_k } Local phase more rigid, but needed to ensure convergence
3. Parameter Update: Update Δ_k
 - $x_{k+1} = x_k + \Delta_k d_k$
 - $\Delta_{k+1} = \Delta_k$

Variations on LEED

❖ LEED

- Multiple scattering model
- I-V spectra computed repeatedly until best-fit structure is found
- Computation time is proportional to the number of parameters

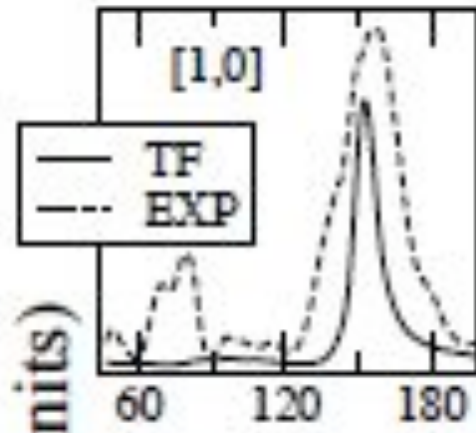
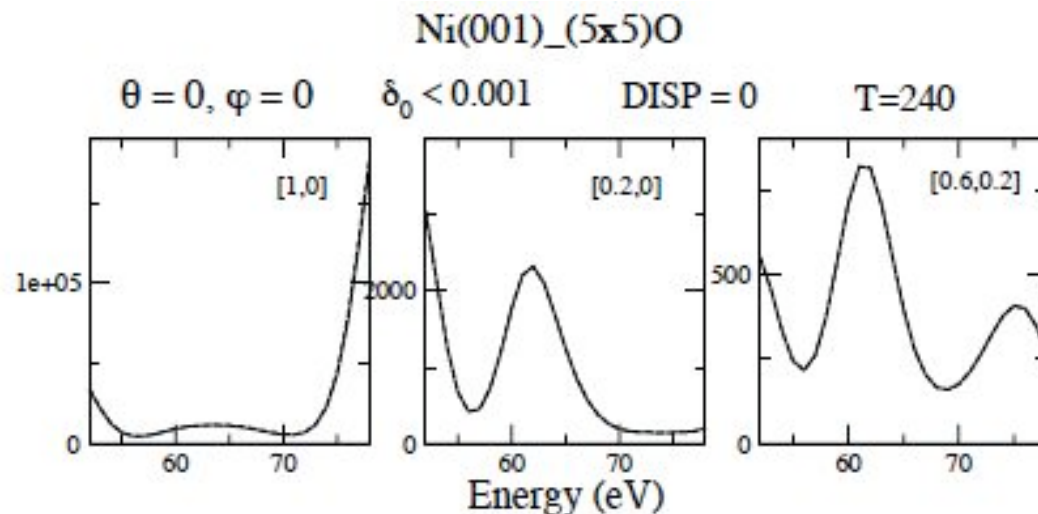
❖ TLEED (Tensor LEED)

- Perturbation method to calculate I-V for a structure close to a reference structure
- For a reference structure use multiple scattering
- Efficient for local modifications (i.e. no categorical variables) - otherwise computationally expensive

Using Kinematic LEED as a simplified physics surrogate (SPS)

- ❖ R-factor depends on:
 - Structural parameters, i.e. atomic positions, chemical identity
 - Non-structural parameters, i.e. inner potential, phase shift δ , thermal effects and damping.
- ❖ KLEED - Kinematic LEED
 - Single scattering model
 - I-V spectra computed in a few seconds
 - Compared to multiple scattering which takes ~ 2 minutes
- ❖ As $\delta \rightarrow 0$, KLEED agrees with multiple scattering

I-V curves for KLEED versus multiple-scattering



- ❖ Ni(001)-(5x5)Li structure
- ❖ KLEED and multiple scattering agree well with small phase shift
- ❖ KLEED agrees well with experimental data as long as the incident angle is close to perpendicular
- ❖ However for larger phase shift there is no guarantee of agreement

Additive Surrogate using a Simplified Physics Surrogate (SPS)

- ❖ Define $\phi_A(x) = \phi_S + \phi_I$
 - where ϕ_A = Additive Surrogate,
 ϕ_S = Simplified Physics Surrogate (SPS),
 ϕ_I = Interpolatory Surrogate

- ❖ Search:

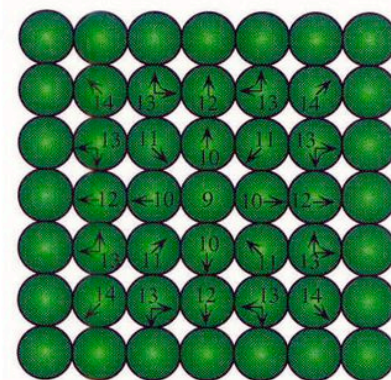
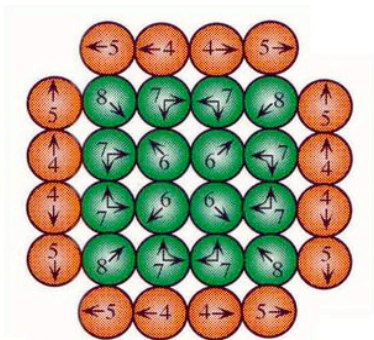
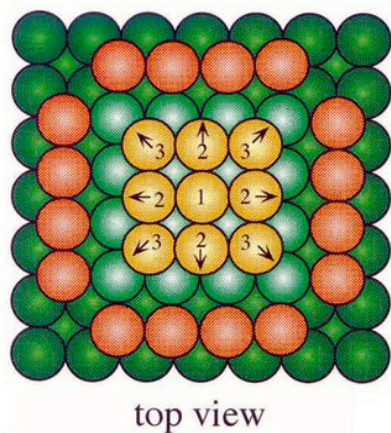
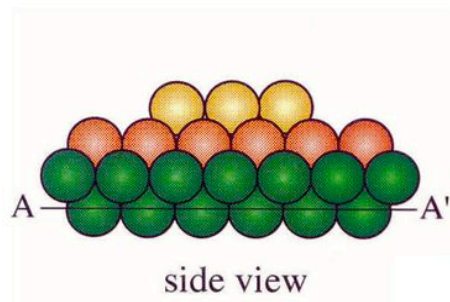
- IF (first time)
 - THEN initialize ϕ_I with LHS
 - ELSE recalibrate ϕ_I with DACE
- Construct Additive Surrogate
- Solve $\min \phi_A = \phi_S + \phi_I$

KLEED

DACE surrogate model of difference
between the SPS and Truth

Test problem

Ni(100)-(5x5)-Li

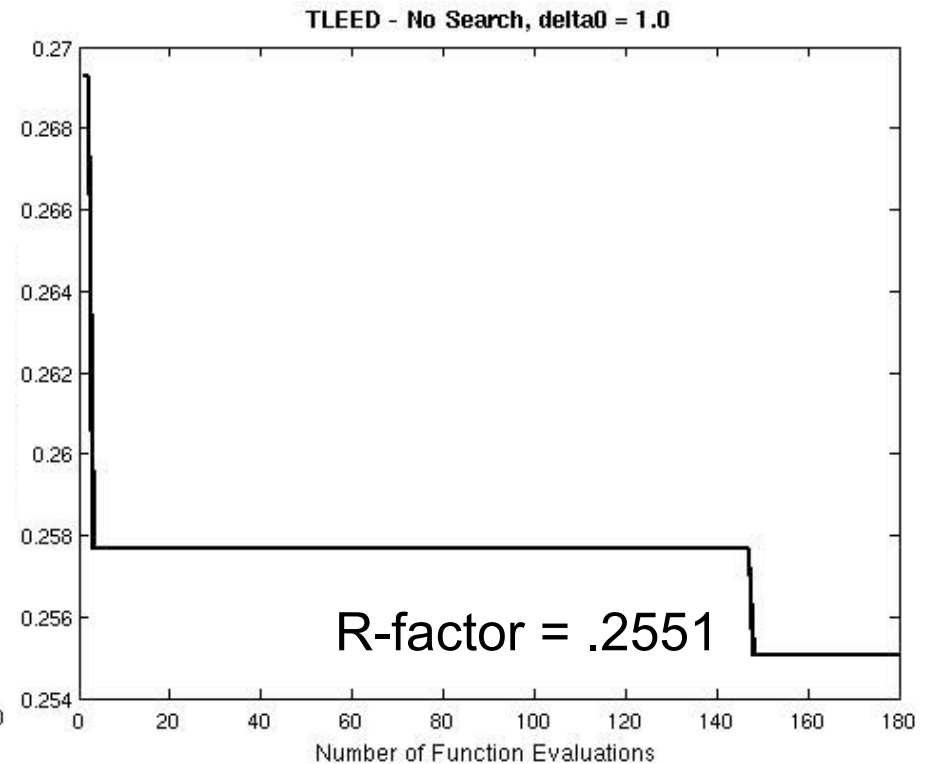
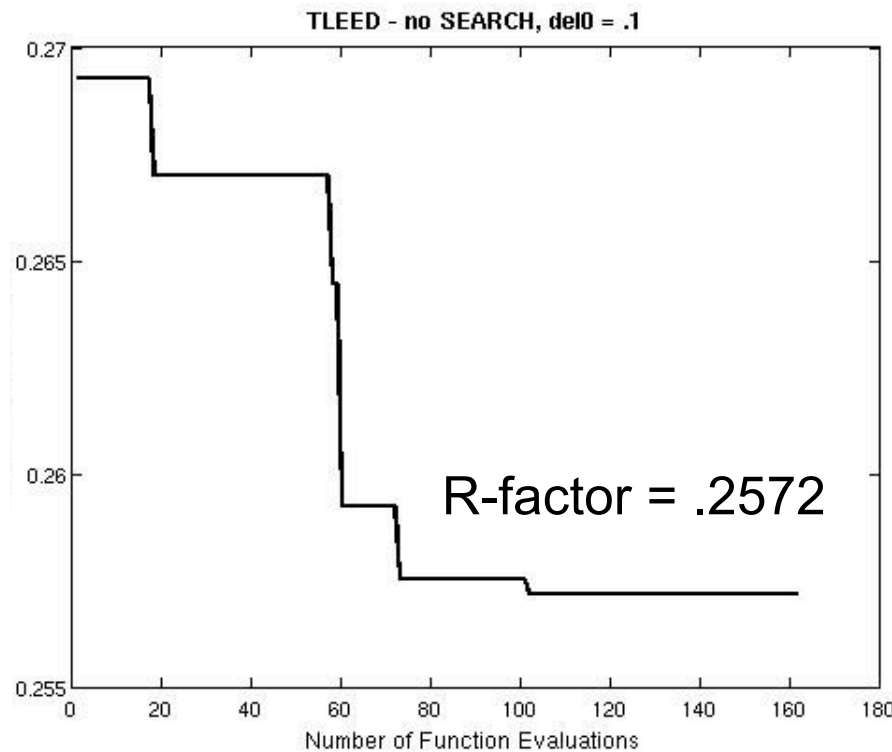


- ❖ Model 31 from set of model problems
- ❖ Three layers
- ❖ 14 atoms
 - 14 categorical variables
 - 42 continuous variables
- ❖ Positions of atoms constrained to lie within a box
- ❖ Used NOMADm:
<http://en.afil.edu/ENC/Faculty/MAbramson/NOMADm.html>

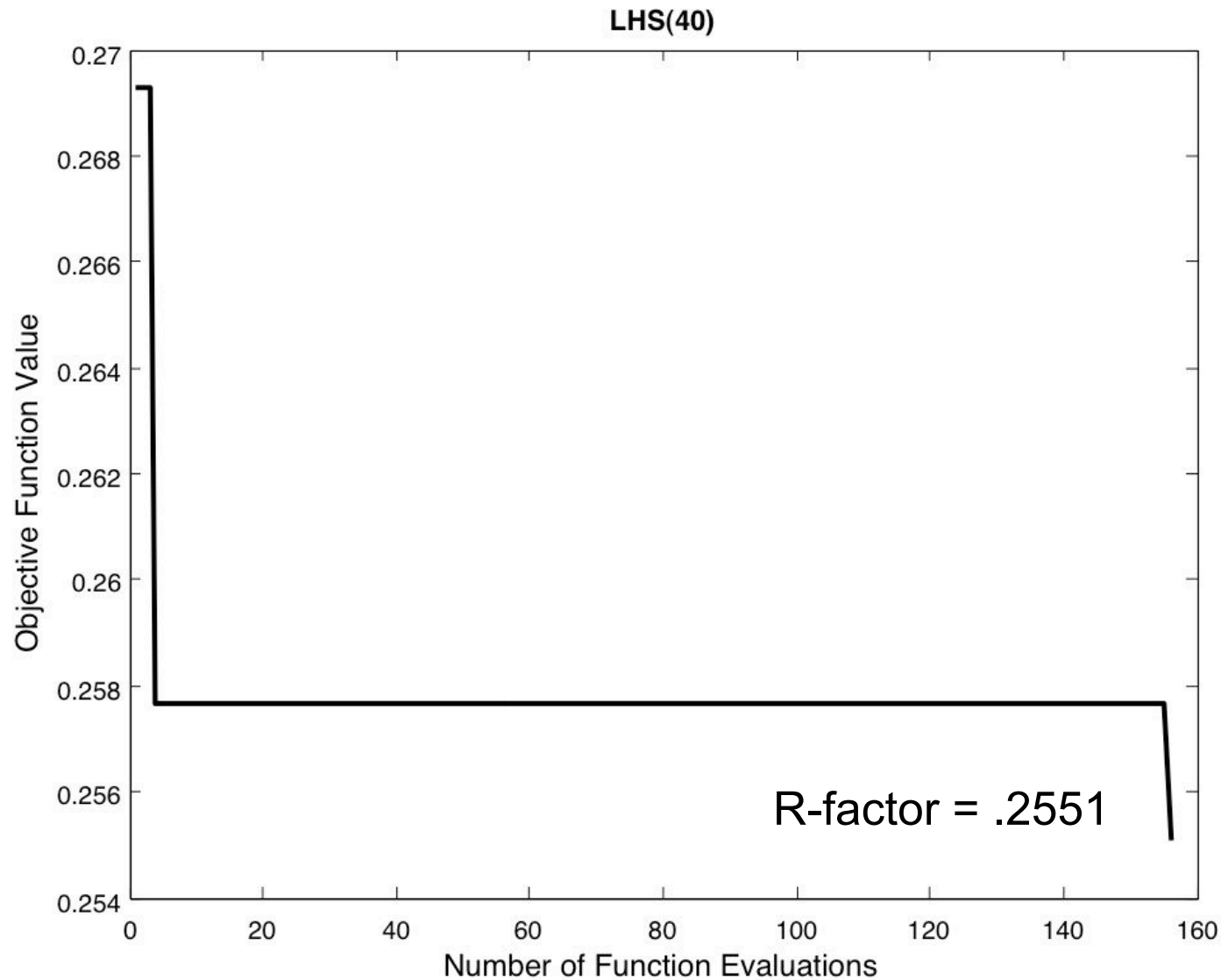
Test cases

- ❖ Start with best known feasible point
- ❖ 3 different approaches
 - No Search Step
 - LHS Search
 - Simplified Physics Surrogate/DACE
 - LHS with 5 and 15 points
 - $\Delta = 1.0$
 - $\Delta = 0.1$

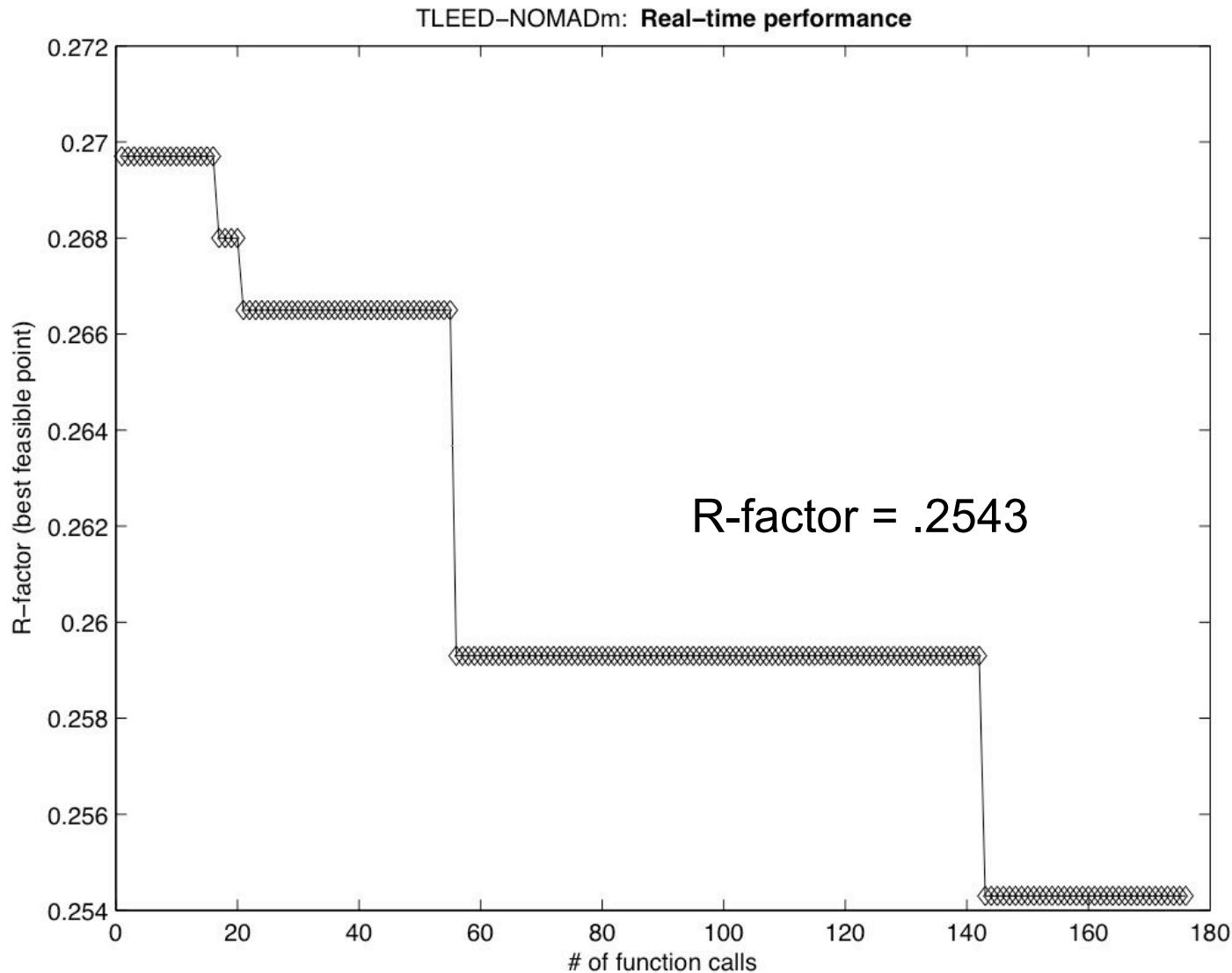
Relaxation of continuous variables using no search phase



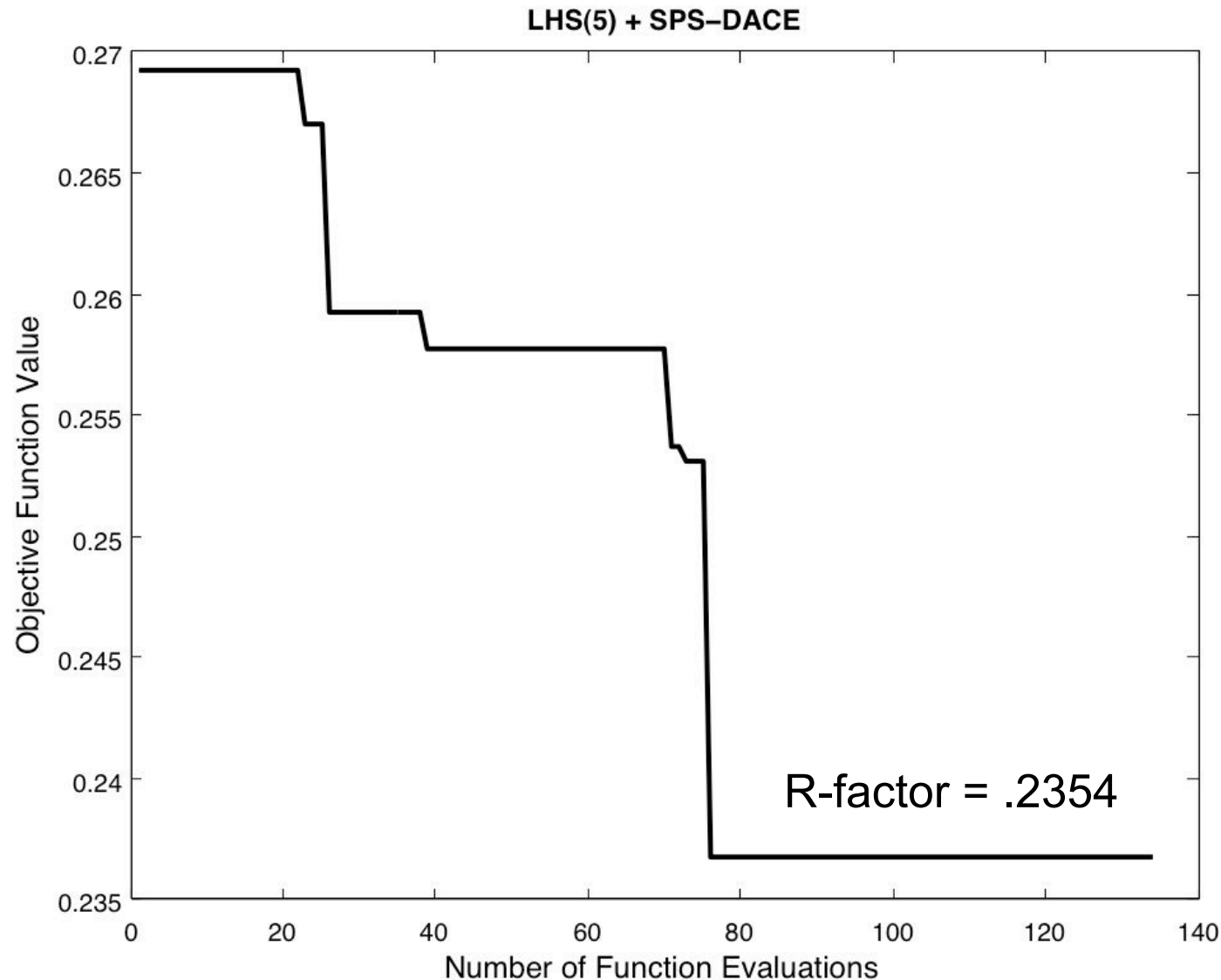
Relaxation of continuous variables using LHS with 40 points



Relaxation of continuous variables using Additive Surrogate, $\Delta_0 = 1.0$



Relaxation of continuous variables using Additive Surrogate, $\Delta_0 = 0.1$



Conclusions

- ❖ Preliminary results indicate that performance can be enhanced by using an additive surrogate function in the search phase
- ❖ Efficiency is highly dependent on various algorithmic parameters
- ❖ Several issues remain before we can declare victory

Future work

- ❖ Explore effect of initial delta, number of LHS points, minimum delta, ...
- ❖ Explore different simplified physics surrogates
- ❖ Add capability for categorical variables

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Mange tak - Thank you

